Holzforschung, 41(4), 239-45 (1987)

The Stereochemistry of β−5 Lignin Model Compounds

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Keywords
β−5 Lignin model compound
Phenylcoumaran
Phenylboronate
Stereochemistry
NMR
X-ray crystallography
Dihydrodehydrodiisoeugenol

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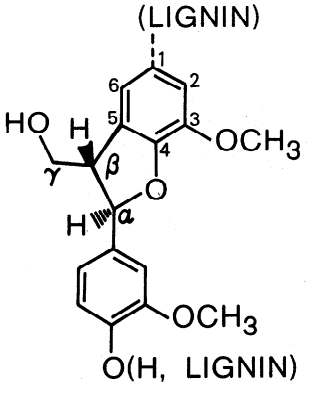
Summary

A range of chemical and spectroscopic techniques were used to determine the stereochemistry of several β−5 lignin model compounds. In phenylboronate derivatives of the model compounds, the torsional angles implied by the ^{1}H NMR coupling constants in the six-membered ring ($J_{\alpha\beta}$ = 4 Hz, $J_{\beta\gamma_{ax}}$ = 10−12 Hz) confirmed their *erythro* stereochemistry. The conformation of the phenylboronates gave rise to shielding, and consequent unusual spectral dispersion of the aromatic lignin dimer protons in their ^{1}H NMR spectra. This allowed the complete assignment of the ^{1}H and ^{13}C NMR spectra by use of the 2D ^{13}C−^{1}H shift correlation pulse sequence. A *threo* acetal of one model was synthesised, but synthesis of the *threo* model itself was not achieved. The ^{1}H NMR spectrum of the *threo* acetal, with $J_{\alpha\beta}$ = 10 Hz, indicated an axial-axial arrangement of Hα and Hβ, which confirmed the *threo* configuration. Also reported is an X-ray diffraction crystal structure of dihydrodehydrodiisoeugenol which confirms the chemically predicted *erythro* stereochemistry.

Introduction

In the course of our studies (Ralph *et al.* 1986) on the reactions of β−5 lignin model compounds with anthrahydroquinone and anthranol, we needed to know the stereochemistry of the lignin model compounds used. The β−5 (or phenylcoumaran) linkage accounts for 9−12% of the intermonomer linkages in softwood lignin (Adler 1977).



For compounds with two adjacent asymmetric carbon atoms, the *erythro/threo* nomenclature is a convenient way to assign relative stereochemistry. A problem exists however in assigning chemically similar groups, since the *erythro/threo* nomenclature is only valid for adjacent asymmetric carbons where there are two pairs of equivalent groups and the third pair is different. Hence for 1,2-diarylpropane-1,3-diols (representing β−5 and β−1 linkages), the two aromatic substituents and the two H-atoms are logically chosen as the two chemically similar pairs; the two conformations are shown in the Fischer projections in Fig. 1. For lignin models of the guaiacylglycerol-β-guaiacyl ether type (representing the β−O−4 linkage in lignin), the α−OH and the β−OAr are chosen as one equivalent pair, the other being the protons. The appropriate Fischer projections are therefore those shown in Fig. 2. Some confusion about these descriptions is apparent in the literature. In a recently published paper (Chen *et al.* 1985), β−1 model compound isomers were misassigned, since the assignments were based on the β-ether *erythro/threo* nomenclature. The unambiguous R/S nomenclature is given in Figs. 1 and 2.

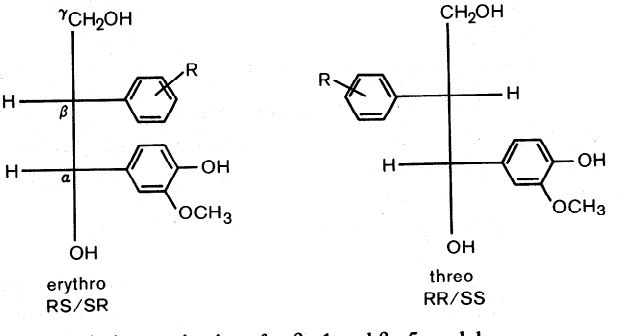


Fig. 1. Fischer projections for β−1 and β−5 models.

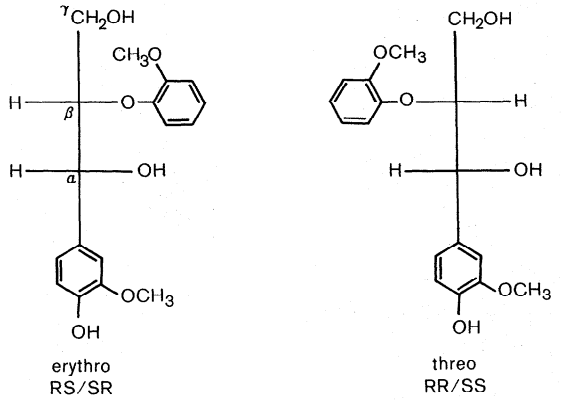


Fig. 2. Fischer projections for β–O–4 models.

The stereochemistry of the propyl sidechains in the β–5 model **1**, synthesised by Brunow and Lundquist, had previously been assigned as *erythro* (Brunow and Lundquist 1984) based on comparisons of the ^{1}H NMR coupling constants of the tetra-acetate with a range of previously synthesised compounds (Kristersson and Lundquist 1980; Ahvonen *et al.* 1983). These assignments were, in turn, based on comparisons of ^{1}H NMR coupling constants with related compounds (Nakatsubo and Higuchi 1975; Ferrand and Huet 1975) whose stereochemistries were determined from NMR spectra of the corresponding phenylboronates or acetals.

While ^{1}H NMR is an excellent diagnostic tool in most cases, it is not always reliable for extrapolating stereochemical assignments over a number of syntheses. ^{1}H NMR coupling constants in aliphatic systems depend, in part, on the torsional angle between vicinal protons. If the molecule exists in an unusual conformation in solution, incorrect stereochemical assignments can result. Further evidence should be obtained to be certain of stereochemical assignments. The syntheses of the acetals (Ralph and Young 1983) or phenylboronates (Nakatsubo and Higuchi 1975) are simple and rapid, and by "locking" the molecule into a six-membered ring, the dihedral angles implied by the ^{1}H NMR coupling constants allow an unambiguous assignment in most cases.

This paper reports the synthesis and characterisation of phenylboronates **5**–**7** of the β–5 lignin model compounds **2**–**4** and confirms that the stereochemistry of the models is indeed *erythro*.

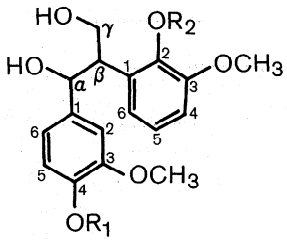
Although we were unable to independently synthesise the *threo* isomer for comparison, the *threo* acetal **8** was obtained by isomerising the *erythro* isomer with $BF_3 \cdot Et_2O$ in the presence of paraformaldeyhde (Ralph and Young 1983).

The preparation of phenylboronates or acetals is only possible if a 1,3-propanediol is present. For phenylcoumaran models such as dihydrodehydrodiisoeugenol **9**, which have two adjacent asymmetric carbons, some confusion as to the stereochemistry has been present in the literature. Conflicting stereochemical predictions have been derived from NMR (Ludwig *et al.* 1964) and chemical (Aulin-Erdtman *et al.* 1963) evidence. We sought to resolve this conflict unambiguously by an X-ray diffraction crystal structure determination of dihydrodehydrodiisoeugenol.

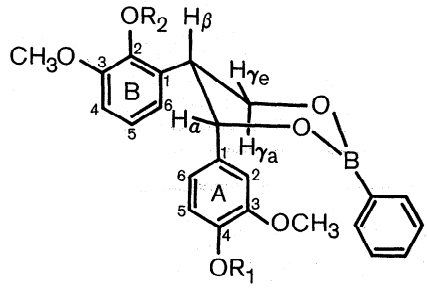
Results and Discussion

Synthesis of β–5 Model Compounds*)

Compound **2** was synthesised by the method of Brunow and Lundquist (1984) and compounds **3** and **4** (see Fig. 3 and footnote) by a modification of this route (Ralph *et al.* 1986). Both syntheses gave single, pure isomers. ^{1}H NMR spectra showed that the β and γ proton resonances were obscured by the methoxyl resonances, particularly in compounds **3** and **4**. More suitable spectral dispersion was obtained from ^{1}H NMR spectra of the acetates of **3** and **4**, but an unambiguous assignment of stereochemistry of any of these was not possible based on NMR evidence, particularly without the other isomer on which to base comparisons. Dihydrodehydrodiisoeugenol **9** was obtain-



1 $R_1 = R_2 = H$ 3 $R_1 = CH_2Ph$, $R_2 = CH_3$
2 $R_1 = R_2 = CH_2Ph$ 4 $R_1 = H$, $R_2 = CH_3$



5 $R_1 = R_2 = CH_2Ph$
6 $R_1 = CH_2Ph$, $R_2 = CH_3$
7 $R_1 = H$, $R_2 = CH_3$

Fig. 3. β–5 lignin model compounds and phenylboronates.

*) Since compounds **2**–**8** contain no substituent in what in lignin units would be the **1** position on the B ring, the B ring is labelled starting from the β–C linkage as in conventional nomenclature.

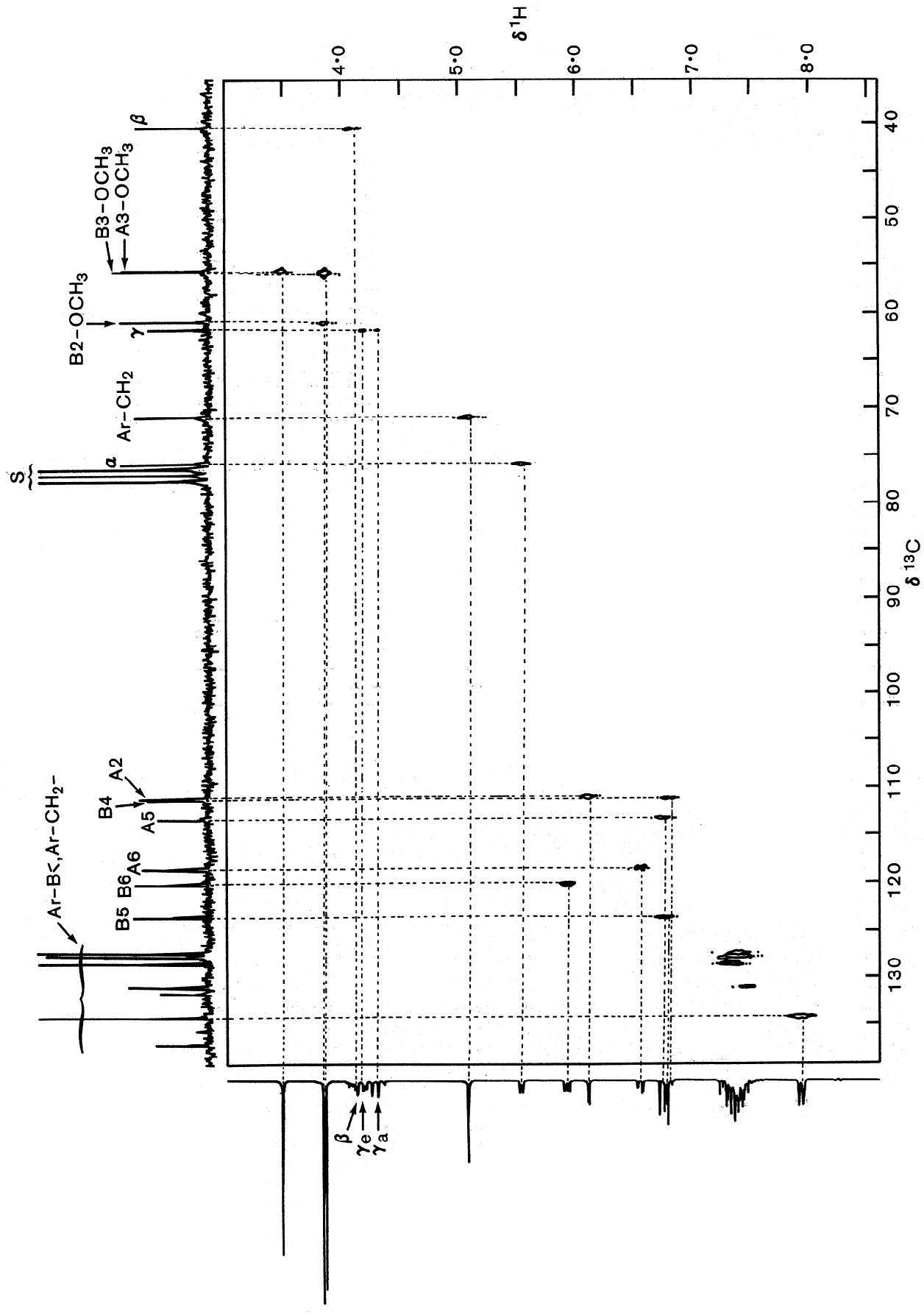


Fig. 4. 2D $^{13}C-^{1}H$ shift correlation spectrum of **6**.

ed from catalytic hydrogenation of dehydrodiisoeugenol (Leopold 1950; Aulin-Erdtman 1942).

Synthesis of Phenylboronates

Phenylboronates **5**, **6**, and **7** (see Fig. 3) were synthesised from models **2**–**4** by the method of Nakatsubo and Higuchi (Nakatsubo and Higuchi 1975). They were obtained as single isomers in quantitative yield.

Characterisation of *Erythro* Phenylboronates

200 MHz ^{1}H NMR spectra of **5**–**7** showed sufficient dispersion of the Hα, Hβ, and Hγ resonances for an unambiguous stereochemical assignment.

For an ideal chair conformation, protons on adjacent carbons are oriented either axial-axial (with a 180° dihedral angle and J ≃ 10 Hz), axial equatorial (60°, J ≃ 3 Hz), or equatorial-equatorial (60°, J ≃ 3 Hz). In compounds **5**–**7**, $J_{\alpha\beta}$ = 4 Hz and $J_{\beta\gamma_{ax}}$ = 10–12 Hz. The αβ coupling constant suggests either an axial-equatorial or equatorial-equatorial orientation, but the large $J_{\beta\gamma_{ax}}$ indicates that Hβ must be axial, hence Hα must be equatorial. This leads to a unique (for phenylboronates of lignin model compounds) axial-equatorial arrangement of the aromatic rings A and B on Cα and Cβ and hence an *erythro* configuration.

An interesting result of this configuration is seen in the ^{1}H NMR spectra. The A ring protons appear to be in the shielding region of the phenyl ring attached to the boron or the B ring, as evidenced by the unusual shifts in **6** of 6.11, 6.74, and 6.55 ppm for protons A2, A5, and A6 respectively. The B ring proton B6 is also extensively shielded (δB6 = 5.92 ppm).

This spectral dispersion of the aromatic protons allows correlation of the ^{1}H and ^{13}C chemical shifts by use of 2D–NMR. ^{13}C–^{1}H NMR shift correlation spectroscopy (Bax and Morris 1981) allows assignment of the ^{13}C chemical shifts based on correlations with the appropriate proton signals. These can be assigned on the basis of their multiplicities and coupling constants (see Fig. 4). In particular it is possible to distinguish between carbons A2 (111.19 ppm) and B4 (111.32 ppm) since proton A2 is a d, δ = 6.11, J_{26} = 2.1 Hz and B4 is a dd, δ = 6.81, J_{45} = 6.0 Hz, J_{46} = 2.7 Hz.

It is even possible from the 2D-spectrum of **6** to fully assign the methoxyl signals in the ^{13}C and ^{1}H spectra. This is aided by the shielding of (presumably) the A3–OCH_3 in the ^{1}H NMR spectrum, and a downfield shift of 5 ppm in the resonance of the sterically crowded B2 methoxyl in the ^{13}C NMR spectrum.

Since ^{13}C nuclei are relatively insensitive to the shielding effects of the diamagnetic aromatic ring currents, it is expected that the ^{13}C shifts in the non-complexed lignin models may also be assigned from this data.

Attempted Synthesis of *threo* **2**

It was possible to obtain low yields of *threo* **2** by $NaBH_4$ reduction of α-ketone **10** (see experimental section), which was obtained by oxidation of *erythro* **2** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Becker and Adler 1961).

$NaBH_4$ reduction of **10** in methanol/OH^- gave a 10:45:45 ratio of *threo* **3**:*erythro* **3**:*erythro* boric acid complex of **3**. Reaction of the crude mixture with phenylboric acid gave 10:90 *threo* **6**:erythro **6**. It was not possible to effect the separation of the two isomers chromatographically as the *threo* isomer degraded on the silica gel.

It was thought that partial conversion of *erythro* to *threo* may be obtained by isomerising *erythro* **2** with $BF_3 \cdot Et_2O$ in the presence of paraformaldehyde to form the acetal (Ralph and Young 1983). ^{1}H NMR examination of the crude reaction mixture showed that >90% conversion to the *threo* acetal **8** had occurred. Although this compound was unstable on silica gel, it was possible to isolate by preparative layer chromatography pure *threo* **8** (see Fig. 5).

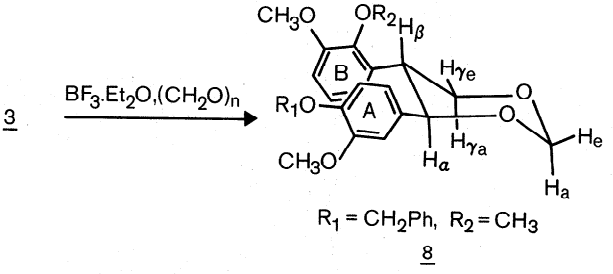


Fig. 5. Synthesis of *threo* acetal **8**.

Characterisation of *threo* **8**

The major evidence for the *threo* conformation is the large (10 Hz) value for $J_{\alpha\beta}$ which is consistent with a diaxial arrangement of Hα and Hβ on the six-membered ring.

The ^{13}C–^{1}H shift correlation spectrum of **8** confirmed the chemical shift assignments. In this case, it was shown that the shielded methoxyl resonance in the ^{1}H NMR spectrum was due to the B2–OCH_3 (cf. compound **6**).

Crystal Structure of Dihydrodehydrodiisoeugenol **9**

Colourless needles of **9** suitable for a crystallographic study were obtained by recrystallisation from petroleum ether (100–120°C). Analysis (see Fig. 6) showed that the crystal contained molecules of $C_{20}H_{24}O_4$ held together within the crystal by hydrogen bonds involving the hydroxyl group, as shown in the stereographic projection of the unit cell (Fig. 7).

It is clear from Figure 6 that the dihydrobenzofuran ring of **9** is twisted from planar, giving rise to a torsional angle of ca. 145° for H7 and H8 (Hα and Hβ in conventional nomenclature). The *erythro* (transoid) stereochemistry is also clear. The torsional angle may explain the $J_{\alpha\beta}$ = 9.7 Hz observed in the ^{1}H NMR spectrum. Based on a simplistic Karplus treatment, a *threo* (cisoid) conformation would be expected from a large coupling constant (implying a dihedral angle of 0° or 180°). The Karplus equation however, was derived for substituted ethanes and is not valid for a highly substituted 5-membered ring containing a heteroatom. It should be noted that the solution conformation (giving rise to the ^{1}H NMR coupling constants) may not necessarily be identical to the solid-state arrangement.

Conclusions

The synthesis of the phenylboronates **5**–**7** of β–5 lignin models **2**–**4** has shown that the stereochemistry is

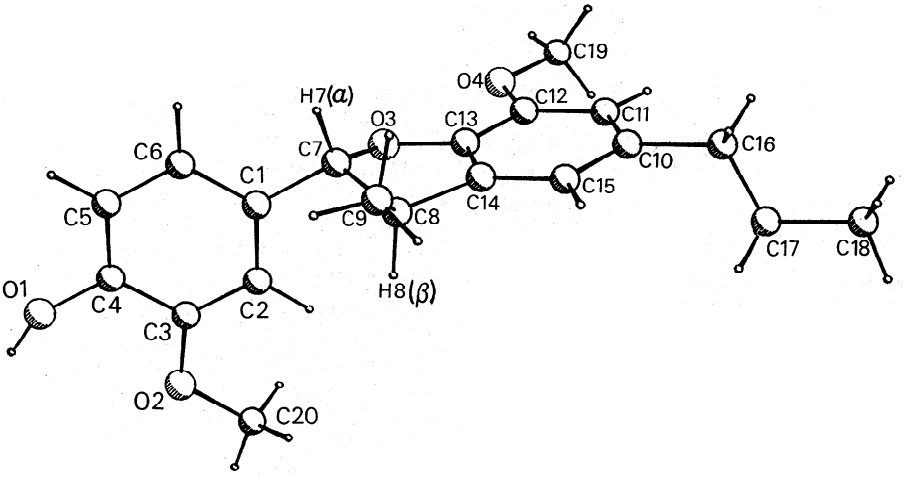


Fig. 6. X-ray structure of **9**.

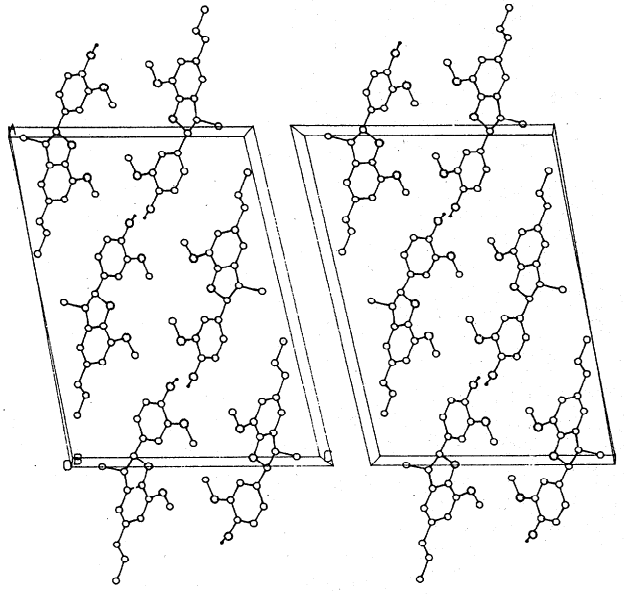


Fig. 7. Stereographic projection of unit cell of **9**.

indeed *erythro* as previously reported (Brunow and Lundquist 1984). The evidence for the configuration (coupling constants in a 6-membered ring) is more conclusive than that obtained from non-rigid propane-1,3-diacetates. Unfortunately, final confirmation from the phenylboronate of an independently synthesised *threo* isomer was not available.

In the case of dihydrodehydrodiisoeugenol **5**, where NMR evidence did not fit well with chemical evidence, the X-ray structure proved the chemically predicted *transoid* configuration.

Experimental

^{1}H NMR spectra were obtained on a Bruker AC200 FT NMR spectrometer. Samples were dissolved in $CDCl_3$ and referenced to internal tetramethylsilane (δ = 0 ppm). Spectra were acquired over 16 K data points zero filled to 32 K, resulting in J values accurate to 0.15 Hz. Lorentzian to Gaussian transformation was employed to improve spectral resolution.

^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker AC200 at 50 MHz. Assignment ambiguities were resolved where possible by use of the ^{1}H decoupled DEPT pulse sequence (Doddrell *et al.* 1982). Spectra were assigned on the basis of the chemical shifts, multiplicities, by comparison with spectra of related lignin model compounds, and from information in the heteronuclear shift correlation spectra.

The ^{13}C–^{1}H shift correlation spectra (Bax and Morris 1981) were obtained on a Bruker AC200 using the Bruker pulse program XHCORR. Parameters: 1 K data points in F_2 (^{13}C) domain, 256 data points zero-filled to 512 in F_1 (^{1}H) domain, recycle delay = 2 s, 96 scans for each experiment, with 256 experiments. Lorentzian-Gaussian resolution enhancement was applied in both domains. Correlation peaks were obtained for all non-quaternary carbons.

Crystal and Molecular Structure of **9**

A colourless needle was obtained by recrystallisation from petroleum ether (100–120°C). Preliminary precession photography indicated a monoclinic space group. Lattice parameters were obtained from the setting angles of 25 reflections centred on an Enraf-Nonius CAD4 diffractometer using monochromated Mo–K_α X-radiation.

Crystal Data

$C_{20}H_{24}O_4$, Mr = 328; Monoclinic, space group $P2_1/a$ (a non-standard setting of $P2_1/c$), **a** = 22.229 (3), **b** = 5.008 (1), **c** = 16.811 (2), β = 103.60 (1), U = 1819.1 A^3 D_c = 1.197 g cm^{-3} for Z = 4. F(000) = 696e, μ(Mo–Kα) = 0.5 cm^{-1}, T = 23°C.

Intensity data were collected in the range $0.5° < \theta < 25°$ using an ω–2θ scan technique. The data were corrected for Lorentz, polarisation and absorption (by an azimuthal scan method). Of the 2211 unique reflections 1140 had $I > 2\sigma(I)$ and were used in all calculations.

The structure was solved by direct methods (Sheldrick 1976). In the final full-matrix least-squares refinement, non-ring atoms were assigned anisotropic temperature factors, ring atoms were treated isotropically and hydrogen atoms were included in calculated positions with common isotropic temperature factors for each type of hydrogen. The refinement converged with R = 0.0694, R_w = 0.0692 where $w = 3.0\,[\sigma^2(F) + 0.001F^2]^{-1}$ with no parameter shifting by more than 0.1σ. A final difference map showed no peaks greater than 0.24 eA^{-3}.

Table 1 Final atomic positions of **9**

ATOM	X/A	Y/B	Z/C
C(1)	0.5688(3)	0.181(1)	0.3023(4)
C(2)	0.5670(3)	-0.015(1)	0.3594(4)
C(3)	0.6211(3)	-0.103(2)	0.4117(4)
C(4)	0.6780(3)	-0.006(2)	0.4051(4)
C(5)	0.6801(3)	0.187(2)	0.3486(4)
C(6)	0.6255(3)	0.284(2)	0.2967(4)
C(7)	0.5111(3)	0.288(1)	0.2478(4)
C(8)	0.4674(3)	0.085(2)	0.1947(4)
C(9)	0.4846(3)	0.024(2)	0.1138(5)
C(10)	0.2985(3)	0.334(2)	0.1507(4)
C(11)	0.3071(3)	0.519(2)	0.2145(4)
C(12)	0.3664(3)	0.556(2)	0.2661(4)
C(13)	0.4137(3)	0.405(1)	0.2511(4)
C(14)	0.4060(3)	0.220(1)	0.1892(4)
C(15)	0.3476(3)	0.181(2)	0.1382(5)
C(16)	0.2340(3)	0.297(2)	0.0944(5)
C(17)	0.1985(4)	0.085(2)	0.1148(6)
C(18)	0.1342(4)	0.052(3)	0.0601(6)
C(19)	0.3308(4)	0.893(2)	0.3460(5)
C(20)	0.5692(4)	-0.385(2)	0.4882(5)
O(1)	0.7310(2)	-0.100(1)	0.4552(3)
O(2)	0.6253(2)	-0.291(1)	0.4722(3)
O(3)	0.4741(2)	0.4240(9)	0.2963(2)
O(4)	0.3802(2)	0.736(1)	0.3288(3)

Final atomic positions are given in Table 1. Lists of bond lengths, bond angles, thermal parameters, hydrogen atom positions, and structure factors may be obtained from the authors on request.

Synthetic Methods

Compound **2** was synthesised following the method of Brunow and Lundquist (Brunow and Lundquist 1984), in 30% overall yield.

Compounds **3** and **4** were synthesised as described previously by a modification of the above route (Ralph *et al.* 1986).

Phenylboronates **5–7** were synthesised by the method of Nakatsubo and Higuchi (Nakatsubo and Higuchi 1975). Dihydrodehydrodiisoeugenol **9** was obtained from the Pd/C catalysed hydrogenation of dehydrodiisoeugenol in quantitative yield (Leopold 1950; Aulin-Erdtman 1942). All exhibited a single spot on analytical tlc (developed in $CHCl_3$) and were clear, colourless oils.

Compound **5**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.51 (3H, s, A3−OCH_3), 3.90 (3H, s, B3−OCH_3), 3.96 (1H, ddd, $J_{\alpha\beta}$ = 4.9, $J_{\beta\gamma e}$ = 4.0, $J_{\beta\gamma a}$ = 12.2, Hβ), 3.98 (1H, dd, $J_{\gamma e\gamma a}$ = 12.2, $J_{\gamma e\beta}$ = 4.0, $H\gamma_e$), 4,19 (dd, $J_{\gamma a\gamma e}$ = 12.2, $J_{\gamma a\beta}$ = 12.2, $H_{\gamma a}$), 4.96 (1H, d, J = 11.3 B2-benzyl CH, 5.08 (2H, d, A4-benzyl CH_2), 5.12 (1H, d, J = 11.3 B2-benzyl CH), 5.37 (1H, br d, $J_{\alpha\beta}$ = 4.9, Hα), 5.88 (1H, dd, J_{56} = 7.3, J_{46} = 2.1, B6), 6.09 (1H, d, J_{26} = 2.1, A2), 6.50 (1H, dd, J_{56} = 8.2, J_{26} = 2.1, A6), 6.75 (1H, d, J_{56} = 8.2, A5), 6.81 (1H, dd, J_{45} = 8.5, J_{56} = 7.3, B5), 6.84 (1H, dd, J_{45} = 8.5, J_{46} = 2.1, B4), 7.20–7.60 (13H, m, Ar−H), 7.90 (2H, dd, J = 7.3, J = 1.7, boron phenyl H2, H6).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 40.48 (Cβ), 55.66 (A3−OCH_3), 55.80 (B3−OCH_3), 61.97 (Cγ), 71.07 (A4-benzyl CH_2), 74.83 (B2-benzyl CH_2), 75.77 (Cα), 111.28 (A2, B4), 113.42 (A5), 118.62 (A6), 120.32 (B6), 123.69 (B5), 127.32 (A4-benzyl C3, C5), 127.65 (boron phenyl C3, C5), 127.80 (A4-benzyl C4), 128.00 (B2-benzyl C4), 128.18 (B2-benzyl C3, C5), 128.31 (B2-benzyl C2, C6), 128.49 (A4-benzyl C2, C6), 130.84 (boron phenyl C4), 131.31 (A1), 131.61 (B1), 134.11 (boron phenyl C2, C6), 137.11 (A4-benzyl C1), 137.46 (B2-benzyl C1), 145.83 (B2), 147.38 (A3), 148.63 (A4), 152.64 (B3).

Compound **6**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.49 (3H, s, A3−OCH_3), 3.84 (3H, s, B2−OCH_3), 3.86 (3H, s, B3−OCH_3), 4.07 (1H, ddd, $J_{\alpha\beta}$ = 4.2, $J\beta\gamma_a$ = 10.2, $J\beta\gamma_e$ = 4.0, Hβ), 4.19 (1H, dd, $J\gamma_a\gamma_e$ = 10.5, $J\gamma_e\beta$ = 4.0, $H\gamma_e$), 4.31 (1H, dd, $J\gamma_a\gamma_e$ = 10.5, $J\gamma_a\beta$ = 10.2, $H\gamma_a$), 5.07 (2H, s, benzyl CH_2), 5.53 (1H, br d, $J_{\alpha\beta}$ = 4.2, Hα), 5.92 (1H, dd, J_{46} = 2.7, J_{56} = 6.72, B6), 6.11 (1H, d, J_{26} = 2.1, A2), 6.55 (1H, dd, J_{56} = 8.3, J_{26} = 2.1, A6), 6.74 (1H, d, J_{56} = 8.3, A5), 6.77 (1H, dd, J_{56} = 6.7, J_{45} = 6.0, B5), 6.81 (1H, dd, J_{45} = 6.0, J_{46} = 2.7, B4), 7.20–7.60 (8H, m, Ar−H), 7.93 (2H, dd, J = 7.7, J = 1.6, H2, H6 on boron phenyl).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 40.52 (Cβ), 55.63 (A3−OCH_3), 55.75 (B3−OCH_3), 60.93 (B2−OCH_3), 61.86 (Cγ), 71.06 (benzyl CH_2), 75.89 (Cα), 111.19 (A2), 111.32 (B4), 113.46 (A5), 118.57 (A6), 120.12 (B6), 123.62 (B5), 127.32 (benzyl C3, C5), 127.7 (boron phenyl C3, C5), 127.80 (benzyl C4), 128.47 (benzyl C2, C6), 130.81 (A1), 130.92 (boron phenyl C4), 131.54 (B1), 134.12 (boron phenyl C2, C6), 137.10 (benzyl C1), 147.30 (B2), 147.40 (A3), 148.66 (A4), 152.59 (B3).

Compound **7**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.53 (3H, s, A3−OCH_3), 3.87 (3H, s, B2−OCH_3), 3.88 (3H, s, B3−OCH_3), 4.11 (1H, ddd, $J_{\alpha\beta}$ = 4.4, $J\beta\gamma_a$ = 10.8, $J\beta\gamma_e$ = 4.0, Hβ), 4.16 (1H, dd, $J\beta\gamma_e$ = 4.0, $J\gamma_a\gamma_e$ = 10.8, $H\gamma_e$), 4,33 (1H, dd, $J\beta\gamma_a$ = 10.8, $J\gamma_a\gamma_e$ = 10.8, $H\gamma_a$), 5.49 (1H, br s, Ar−OH), 5.52 (1H, br d, $J_{\alpha\beta}$ = 4.4, Hα), 5.94 (1H, dd, J_{46} = 3.0, J_{56} = 6.4, B6), 6.115 (1H, d, J = 1.9, A2), 6.535 (1H, dd, J_{56} = 8.2, J_{26} = 1.9, A6), 6.77 (1H, d, J_{56} = 8.2, A5), 6.79 (1H, dd, J_{45} = 8.2, J_{56} = 6.4, B5), 6.82 (1H, dd, J_{45} = 8.2, J_{46} = 3.0, B4), 7.35–7.60 (3H, m, Ar−H), 7.945 (2H, dd, J = 7.7, J = 1.6, H2, H6 on boron phenyl).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 40.55 (Cβ), 55.68 (A3−OCH_3), 55.76 (B3−OCH_3), 60.95 (B2−OCH_3), 61.86 (Cγ), 75.96 (Cα), 109.93 (A2), 111.30 (B4), 113.63 (A5), 119.41 (A6), 120.14 (B6), 123.59 (B5), 127.70 (boron benzyl C3, C5), 130.30 (A1), 130.90, 130.92 (boron phenyl C4), 134.13 (boron phenyl C2, C6), 144.92 (A4), 145.60 (A3), 147.33 (B2), 152.59 (B3).

Compound **8**

Compound *erythro* **2** (80 mg, 0.189 mmole) was dissolved in CH_2Cl_2 (5 ml). To this was added $BF_3 \cdot Et_2O$ (8 mg, 0.047 mmole) and paraformaldehyde (10 mg, 0.340 mmole) and the reaction was stirred for 2 hours at room temperature. The mixture was poured into $CHCl_3$ and washed with saturated $NaHCO_3$. The chloroform solution was dried ($MgSO_4$) and removed under reduced pressure to give a clear oil (80 mg, 98%). Preparative layer chromatography (60% ethyl acetate: pet. ether) gave *threo* **8** (37 mg, 46%).

^{1}H NMR (200 MHz, $CDCl_3$, ^{13}C correlations included) δ: 3.31 (3H s, B2−OCH_3, 60.51), 3.74 (3H, s, OCH_3, 55.82), 3.77 (3H, s, OCH_3, 55.93), 3.78 (1H, ddd, $J\beta\gamma_a$ = ?, $J\beta\gamma_e$ = 3.3, $J_{\beta\alpha}$ = 9.8, β, 41.82), 3.83 (1H, dd, $J\gamma_a\gamma_e$ = 9.7, $J\gamma_a\beta$ = ?, $H\gamma_e$, 71.78, (Cγ)), 4.11 (1H, dd, $J\gamma_a\gamma_e$ = 9.7, $J\gamma_e\beta$ = 3.3, $H\gamma_e$, 71.78 (Cγ)), 4.77 (1H, d, $J_{\alpha\beta}$ = 9.8, α, 83.05), 4.99 (1H, d, J = 6.4, acetal H_{ax}, 94.14), 5.04 (2H, s, benzyl CH_2, 70.92), 5.31 (1H, d, J = 6.4, acetal H_{eq}, 94.14), 6.50–6.80 (5H, m, A2, B4, A5, A6, B6, 110.62, 111.06, 113.65, 119.23, 120.00), 6.99 (1H, dd, J_{45} = J_{56} = 7.9, B5, 123.72), 7.20–7.40 (5H, m, benzyl Ar−H, 127.7, 128.0, 128.4).

^{13}C NMR (50 MHz, $CDCl_3$, non-correlated quaternary carbons) δ: 131.15 (A1), 132.95 (B1), 137.10 (benzyl C1), 147.47, 147.57 (B2, A3), 149.30 (A4), 152.91 (B3).

1-(4-benzyloxy-3-methoxyphenyl)-2-(2,3-dimethoxyphenyl)-3-hydroxypropan-1-one **10**.

Compound *erythro* **2** (500 mg, 1.179 mmole) was dissolved in dioxane (25 ml). To this was added DDQ (481 mg, 2.122 mmole) and the reaction was stirred overnight. The mixture was poured into ethyl acetate and extracted with saturated $NaHCO_3$ until no colour remained in the organic layer. The organic layer was then dried over $MgSO_4$, and the solvent removed under reduced pressure to give a pale orange oil (490 mg, 98%). This was crystallised from CH_2Cl_2/pet. ether to give pale orange crystals m.p. 74–76°C.

^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.85 (1H br s, γ−OH), 3.81 (3H, s, OCH_3), 3.83 (1H, dd, $J\gamma_1\gamma_2$ = 11.1, $J\gamma_1\beta$ = 4.7, $H\gamma_1$), 3.85 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.27 (1H, dd, $J\gamma_1\gamma_2$ = 11.1, $J\gamma_2\beta$ = 8.4, $H\gamma_2$) 5.11 (2H, s, benzyl CH_2), 5.19 (1H, dd, $J\beta\gamma_1$ = 4.7, $J\beta\gamma_2$ = 8.4, Hβ), 6.60−7.00 (4H, m, Ar−H), 7.20−7.40 (5H, m, Ar−H), 7.55 (1H, dd, J_{56} = 6.5, J_{26} = 2.0, A6), 7.57 (1H, d, J = 2.0, A2).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 48.22 (β), 55.06 (OCH_3), 55.26 (OCH_3), 60.74 (B2−OCH_3), 64.01 (γ), 70.01 (benzyl CH_2), 110.86 (B4), 111.15 (A2), 111.66 (A5), 119.70 (B6), 122.85 (A6), 123.90 (B5), 126.76 (benzyl 3,5), 127.53 (benzyl 4), 128.09 (benzyl 2,6), 129.10 (A1), 130.44 (B1), 135.86 (benzyl 1), 145.71 (B2), 148.74 (A3), 151.97 (A4), 152.57 (B3), 198.06 (α−C = 0).

Acknowledgements

The authors would like to thank Dr. C. Rickard, University of Auckland for collection of the X-ray data, Dr. B.K. Nicholson and Mr. R. Thomson (University of Waikato) for assistance in solving the crystal structure, Dr. L. Main (University of Waikato) and Drs. J.M. Uprichard and I.D. Suckling (Forest Research Institute) for helpful discussions. Funding for R.M.E. through New Zealand Forest Service, Forest Research Institute Postgraduate Study Award # 206 is gratefully acknowledged.

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